

LETTERS
TO THE EDITOR

Ratio between Mono- and Disubstituted Products
of Electrochemical Amination of Aromatic Substrates

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Received January 8, 2002

The indirect cathodic amination of aromatic substrates with the system Ti(IV)–NH₂OH is expedient to perform in concentrated sulfuric acid solutions ([H₂SO₄] > 7 M) [1–3]. In highly concentrated H₂SO₄ media, side reactions of aminocyclohexadienyl radicals are suppressed and the concurrent amination reaction yielding ammonia is decelerated. The final products of the radical-cation amination in such conditions are aromatic diamines.

In the present work we used the example of electrochemical amination of benzene to demonstrate a possibility for selective synthesis of not only di-, but also monoamino derivatives in highly concentrated sulfuric acid solutions.

The electrolysis of the Ti(IV)–NH₂OH–C₆H₆ system was accomplished in a three-electrode glass electrochemical cell with the cathodic and anodic compartments separated by a ceramic diaphragm. The catholyte, 11 M aqueous H₂SO₄ containing 0.1 M titanium(IV) sulfate, 0.2 M hydroxylamine, and acetic acid or acetonitrile, was 25 ml in volume. The substrate was a highly dispersed emulsion of 10 ml of benzene in the catholyte, purged with argon. Titanium(III) was generated on a mercury cathode at a current density of 6 mA/cm² and 40°C. The quantity of electricity consumed in the amination reaction was 250°C.

After electrolysis, the catholyte was cooled and neutralized by successive treatment with saturated aqueous sodium hydroxide and NaHCO₃. The amination products were extracted with benzene and analyzed on a Chrom-4 chromatograph with a flame-ionization detector and a glass column [2500 × 3 mm, 5% XE-60 on Chromaton N-AW-DMCS (0.160–0.200 mm)] operated at 150°C.

In the absence of an organic solvent, the electrochemical amination of benzene gives aniline and *o*- and *p*-phenylenediamines. The current yields of

aniline (Y_c^a) and isomeric phenylenediamines (Y_c^{ph}), on the basis of consumption one electron per one hydroxylamine molecule, are 19.7 and 23.9%, respectively ($Y_c^a/Y_c^{ph} = 0.82$).

Introduction of an organic solvent in the electrolyte much enhances the overall efficiency of the substitution reaction. At the same time, whereas the yield of aniline increases with increasing concentration of the organic solvent, the dependences of the total yield of *o*- and *p*-phenylenediamines on the concentrations of acetic acid and acetonitrile show maxima in 0.5 and 1.7 M solutions (Y_c^{ph} 35.8 and 42.5%), respectively. Therewith, as the fraction of the solvent in the catholyte increases, *m*-phenylenediamine appears among the reaction products. Thus, for instance, the current yields of phenylenediamines in 5 M CH₃CO₂H and 5.5 M CH₃CN are 25.5 and 18.8%, respectively, and the Y_c^a/Y_c^{ph} ratios attain 4.4 and 9.1 (since the electrochemical amination in these media occurs by a chain mechanism, the current yields of aniline and the total yields of mono- and diamino derivatives are higher than 100%), i.e. aniline becomes the major product of the radical-cation substitution at already moderate concentrations of the solvents.

The reduced yields of isomeric phenylenediamines in sulfuric acid solutions containing acetic acid or acetonitrile are probably explained by the well-known ability of these solvents to solvate cations and anions, as well as by the fact that the concentration of basic species B[−] (B[−] = H₂O, HSO₄[−], SO₄^{2−}) decreases as the solvent concentration in the catholyte increases. The presence of CH₃CO₂H or CH₃CN in the solution prevents formation of associates C₆H₅NH₂ · HB whose amination gives rise to *o*- and *p*-phenylenediamines [2].

ACKNOWLEDGMENTS

The work was financially supported by the Russian Foundation for Basic Research (project no. 01-03-33084), as well as the *Fundamental'noe issledovanie i vysshee obrazovanie* Collaborative Program of CRDF and Ministry of Education of the Russian Federation (REC-007).

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